Oxidation of N-benzyl-N-methylhydroxylamines to nitrones. A mechanistic study

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ABSTRACT

Oxidn. of various N- (o-, m-, p- substituted benzyl)-N-methylhydroxylamines has been carried out using mercury(II) oxide and p-benzoquinone (p-BQ) as oxidants. Hammett plots have been obtained with neg. values, showing the development of a pos. center in the transition state. The unstable E nitrones, which readily isomerize to the more stable Z nitrones, are obtained in appreciable quantities and in some cases as the major product. A considerable deuterium isotope effect is obsd. in the oxidn. process. The overall picture of the mechanistic pathway involves electron transfer from nitrogen to the oxidant followed by hydrogen abstraction.